Influence of Iodine Treatment on the Carbonization Behavior of *Antheraea pernyi* Silk Fibroin Fiber

Md. Majibur Rahman Khan, Yasuo Gotoh, Hideaki Morikawa, Mikihiko Miura

Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda, Nagano 386-8567, Japan

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ABSTRACT: The effect of iodine treatment on the carbonization behavior of tussah silk fibroin (SF) fiber from a wild cocoon, *Antheraea pernyi* (*A. pernyi*), was investigated, and the carbon yield, fiber morphology, structural characteristics, and mechanical properties were evaluated. The SF fiber was treated with iodine vapor at 100°C for 12 h and was heated to 800°C under a multistep heating program as carbonization process, which corresponds to the constant thermal degradation rate of SF determined by dynamic thermogravimetric analysis (TGA). The carbon yield was ca. 39 wt %, which is much higher than those for untreated *A. pernyi*. Scanning electron microscopic (SEM) observation showed that obtained carbon fibers from iodinated SF were structurally intact, and the strength was higher than that from untreated SF. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, and Raman spectroscopy revealed that the structures of the carbon fibers obtained from both untreated and iodinated SF were almost the same and amorphous. At the early stage of carbonization of SF, amide bonding of SF molecules was begin to collapse at temperatures higher than 350°C and was completely dissociated by carbonization at 800°C. Dynamic viscoelastic measurements showed that with heating above 270°C the iodine component introduced intermolecular crosslinking of SF and the melt flow of the SF was inhibited, which enhances higher carbon yield and better performance of silk based carbon fiber. J Appl Polym Sci 110: 1358–1365, 2008

Key words: tussah silk biopolymers; carbonization; iodine treatment; structure; mechanical properties

INTRODUCTION

Silkworm silk fibroin (SF) is a typical natural biopolymer produced by two major species of silkworms, domestic *Bombyx mori* (*B. mori*) and wild, and has been highly valued as a textile fiber for thousands of years. *Antheraea pernyi* (*A. pernyi*) is the most familiar species among wild silkworms and is mass-produced in north-east China for silk fiber, namely tussah silk production.[1] The structure and chemical composition of *A. pernyi* SF are different from those of *B. mori* SF. In comparing with domestic SF, the amino acid composition of tussah SF is characterized by the abundant alanine (Ala), aspartic acid (Asp), and arginine (Arg) amino acid residues, and less quantity of glycine (Gly) residue. This composition is related to the abundance of -$(Ala)_n$- sequence, which favors α-helix formation.[2] Furthermore, the amino acid composition of tussah SF is characterized by the abundance of basic [lysine (Lys), histidine (His), and Arg] and acidic [Asp and glutamic acid (Glu)] amino acid residues, and the presence of tripeptide sequence of Arg-Gly-Asp.[3] Based on these structural features, tussah SF is considered as an attractive starting raw material for nontextile applications i.e., for developing innovative applications in biotechnological fields.

As one aim to diversify the new products of SF, the researches concerning the carbonization of silk can be involved. Recently it has been shown that *B. mori* SF fiber is a suitable precursor for producing carbon fibers.[4,5] Silk-based carbons are very promising raw materials for the applications in bio- and electrochemical fields. The carbonized silk materials exhibit antibacterial property and possess multiple numbers of dimples generated by heating on its surfaces and are used as supports for catalysts.[6] Many attempts have been made to develop carbonized silk products or proposed to develop as functional materials, such as carbonized silk powders for coloring coatings, cosmetics, pharmaceuticals,[7] skin external preparations,[8,9] hydrogen storing materials,[10] wound dressing,[11] hazardous substance decomposer,[12] mask,[13] gas adsorbent,[14] etc. Many products are also developed from carbonized silk materials in electrochemical field, for example, carbonized cocoons for fuel cell and electrode materials,[15] double layer capacitors,[16] and electromagnetic shields.[17,18]

Correspondence to: Y. Gotoh (ygotohy@shinshu-u.ac.jp).
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Many researches of tussah SF have been carried out, although the number of reports are considerably smaller compared with those of *B. mori* SF. Especially, the study of carbonization behavior is much minor. Some articles treat the thermal decomposition of tussah SF below 300°C,[19–26] but we only know one article concerning carbonization behavior; that is, Nishikawa et al. reported the carbonization behavior and some characters for mulberry silk and tussah silk.[27]

To produce high performance and high functional carbon materials from polymeric precursors, iodine treatment process has been reported. Iodine has been reported as a good stabilizing agent for producing pitch-derived carbon.[28] Recently, iodine treatment has been expanded to other polymers, such as, polyacrylonitrile,[29] poly(vinyl alcohol),[30] and *B. mori* SF,[4] etc., and resultantly some interesting characters accompanied by high carbon yield were found.

With regarding the structural characteristics of iodinated SF, recent researches revealed that both domestic and tussah SF absorbed polyiodide ions, and the structure and physical properties have been greatly influenced by iodine treatment.[31,32] The iodine absorption behavior of tussah SF is difference to that of domestic SF because of the molecular composition.[32] However, until recently, the influence of the iodine treatment on the carbonization behavior of tussah SF has not been reported yet.

The aim of this study is to investigate the carbonization behavior of iodinated tussah SF, and evaluate the carbon yield, fiber morphology, structure, and the mechanical properties of the obtained carbon fibers by using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, wide angle X-ray diffraction (WAXD), dynamic mechanical thermal analysis (DMTA), elemental analysis, and tensile measurements.

EXPERIMENTAL

Materials

A. pernyi cocoon fiber provided by Dainippon Silk Foundation, Japan, was first degummed to remove sericin. The degumming process was performed by standard marseille soap/soda ash method,[33] maintaining the following steps:

i. Prewash: distilled water, 40°C, 30 min.
ii. Primary degumming: 15–20% of marseille soap, liquor ratio of 100 : 1, 97–99°C, 2 h.
iii. Post degumming: 1.0% of sodium carbonate, liquor ratio of 100 : 1, 80–90°C, 10–15 min.
iv. Redegumming: 0.5% of sodium carbonate, liquor ratio of 100 : 1, 50–60°C, 10–15 min.
v. Final rinsing and drying: thoroughly rinsed with copious quantities of warm distilled water followed by rinsing in cold water, dried immediately at 80°C for 1 h, and then kept at room temperature for 48 h.

After degumming, Soxlhet extraction was conducted using methanol to remove foreign particles.

Iodine treatment

The iodine treatment of tussah SF fiber was performed by the following procedure: the degummed tussah SF fiber was dried in an oven, and the weight was measured in dry condition. Then the fiber was enclosed with an adequate amount of iodine in a small test tube in a glass vessel. After sealing the glass vessel, it was placed in an oven heated at 100°C, where iodine was vaporized and kept for several periods. After the treatment, the color of SF fiber turned to dark brown. Finally, the weight of iodinated samples was measured. The iodine absorption percentage was calculated by measuring the weight change of the SF fibers before and after the iodine treatment.

Carbonization process

Prior to carbonization of SF, to control the thermal degradation of SF fiber, dynamic thermogravimetric analysis (dynamic TGA) was performed using the constant reaction control (CRC) mode at −0.001 wt % s^{-1} of constant weight reduction rate from room temperature to 800°C with a Rigaku Thermo plus II TG 8120 under an Ar atmosphere. Figure 1 shows the dynamic TGA result of untreated tussah SF fiber. The solid and broken lines indicate temperature profile and TG curve, respectively. According to this result, we defined a multi steps heating schedule for carbonization as shown in Figure 2. The untreated and iodinated specimens were heated from 25 to

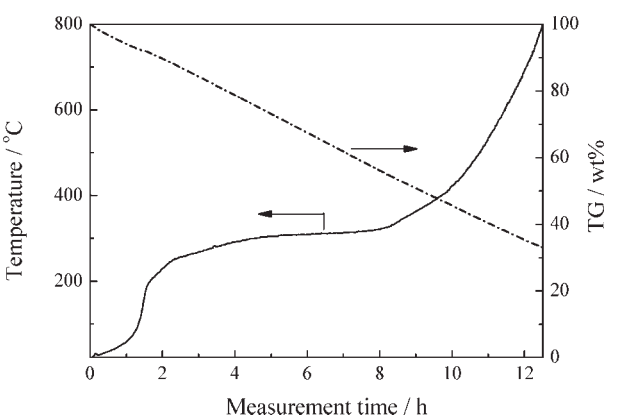

Figure 1 Dynamic TGA curve and temperature profile of untreated tussah SF fiber under control mode at a constant reaction rate of 0.001% s^{-1}.

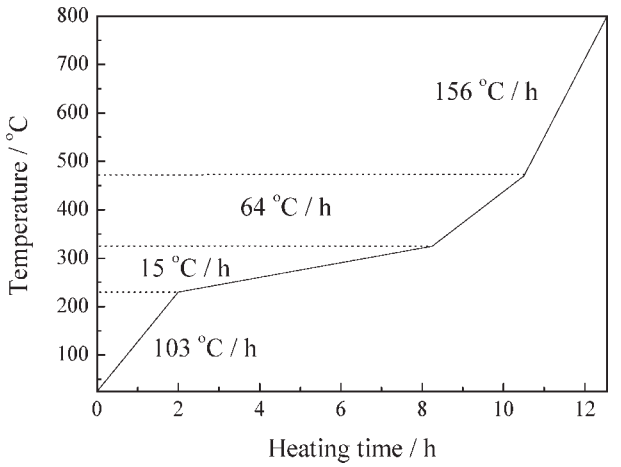

Figure 2 Multistep heating schedule determined according to dynamic TGA result (Fig. 1) of untreated tussah SF.

800°C in a tubular furnace under an Ar gas flow using the multistep heating condition.

Measurements

A normal TGA was carried out from room temperature to 800°C at a heating rate of 5°C min^{-1} with a Rigaku Thermo plus II TG 8120 under an Ar atmosphere.

The morphologies of the fibers were observed with a Hitachi S-2380N SEM at 15 kV of acceleration voltage. Before placing the samples in the SEM chamber, the samples were mounted onto an aluminum stud and sputter-coated with platinum for 180 s to prevent electron charge up.

FTIR spectroscopy was measured with a Shimadzu FTIR-8400S in the region of 4000 cm^{-1}–400 cm^{-1} at room temperature. The fibers were crushed by pulverization in the frozen state using liquid nitrogen and measured by KBr method.

WAXD profile was obtained by a Rigaku Rotorflex RU-200B and a diffractometer using Ni-filtered CuKα radiation generated at 40 kV and 150 mA.

Raman spectroscopy was measured by S. T. Japan, Inc. HoloLab-5000, equipped with a MK-II filtered probe head using Nd: YAG (Yttrium Aluminum Garnet) laser beam of 532 nm generated at 50 mW. The measurement was carried out under the conditions of resolution of 2.5 cm^{-1}, exposure time of 10 s, and summation time of 10.

DMTA was measured using an ITK Co. DVA-225 at the stretching mode, frequency of 10 Hz, and a heating rate of 10°C min^{-1}.

The CHN elemental analysis was performed on a Parkin-Elmer 2400 II analyzer.

The tensile properties were measured with an Orientec Co. Ltd., Japan, Tensilon Model RTC 1250A at 22°C and 65% RH at a gauge length of 40 mm and a strain rate of 100% min^{-1}.

We used SF fibers treated with iodine vapor at 100°C for 12 h for each measurement.

RESULTS AND DISCUSSION

Iodine absorption and crosslinking

Amino acid composition and structural characteristics of tussah SF are different from those of *B. mori* SF. Therefore, iodine absorption behavior is expected to be different between them. The iodine-sorption percentage of tussah SF fibers is shown as a function of iodine treatment duration in Figure 3. The weight of the SF fibers increased rapidly with iodine treatment time. After 12 h, the iodine content was achieved to 46 wt % by introduction of iodine component into the fibroin. Then, the trend of weight increasing was changed to slow and the content reached at 57 wt % after 24 h. The iodine-absorption content of tussah SF is comparatively higher than that of *B. mori* SF.[4] Higher iodine-absorption power of tussah SF seems to be related to difference in not only the amount of basic and acidic amino acid residues of SF molecules but also in the higher-order structures. To elucidate the crosslinking of SF with polyiodide ions, DMTA measurement has been carried out.

Figure 4 shows the temperature dependence of the storage modulus (E') for untreated and iodinated tussah SF fibers. The storage modulus of untreated specimen increases gradually with temperature up to 110°C, owing to the evaporation of water sorbed in the fiber. The E' curve then remains constant until around 210°C, followed by a gradual decrease, and then exhibits a sharp fall around 280°C, which is attributed to the collapse of the fiber lapsed because of the melting of the crystallites. On the contrary, the thermal stability of fibers decreased significantly by introduction of polyiodide ions into SF molecules.

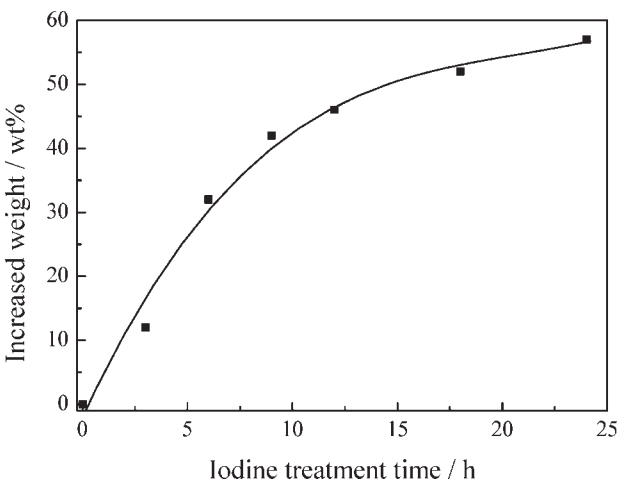

Figure 3 Increased weight by sorption of iodine in tussah SF fiber at different iodine treatment times.

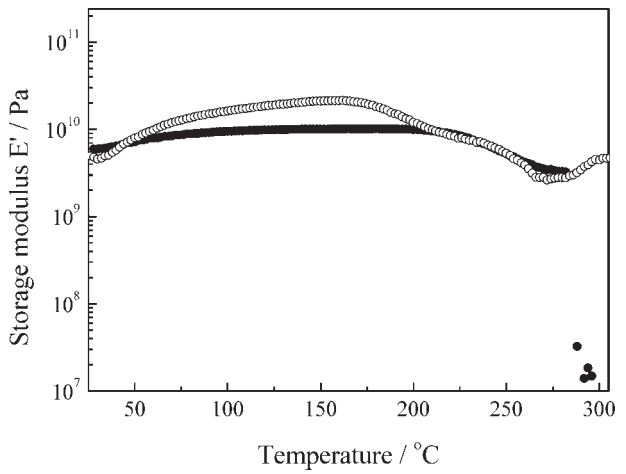

Figure 4 Temperature dependence of storage modulus for tussah SF fiber treated with iodine vapor at 100°C for 12 h; (•) untreated specimen, (○) iodinated specimen.

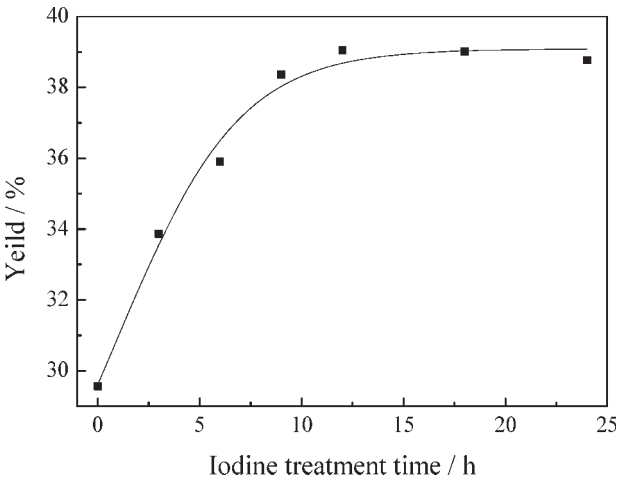

Figure 5 Relationship between iodine treatment time and the yield of tussah SF fiber carbonized at 800°C.

The first fall of onset temperature is shifted to lower temperature at ~ 162°C than that observed for the untreated specimen at ~ 213°C. These changes of E' behavior may be attributed to the effect of introduction of polyiodide ions into fiber segments, which remained within the fiber matrix long enough causes SF molecular motion to occur more easily with heat, and consequent softening of the SF molecules. Above 270°C, the iodinated specimen shows the increase of E' (i.e., the stiffness is increased) restricting the melt-flowing of fibers, which implies the formation of intermolecular crosslinking accompanied by the hardening of the sample. Although the reason for the formation of crosslinking has not yet been determined, it is most likely related to the iodine component.

Carbonization behavior and carbon yield

An important aspect in carbon fiber production is the yield of residual carbon from polymeric precursor. In general, lower yield results in higher production cost and lower mechanical property. The relationship between the carbon yield and iodine treatment time is shown in Figure 5. In case of untreated specimen, the carbon yield was 29 wt %. For iodine-treated specimens, the carbon yield obtained at 800°C gradually increased and saturated at 39 wt % over 12 h of the treatment time. In the case of *B. mori* SF, the carbon yields from untreated and iodinated SFs carbonized under the same condition were 29 wt % and 36 wt %, respectively.[4] The higher carbon yield from tussah SF was a meaningful difference compared with *B. mori* SF, and the effect of the iodination was higher for tussah SF. This should be related to the different molecular structure based on amino acid composition of SF and high-order structure, which lead to the difference of iodine sorption behavior.[32]

To investigate the thermal decomposition behavior of iodinated SF, TGA measurement was performed. Figure 6 shows TGA curves of untreated and iodinated tussah SF fibers. The measurement conditions of TGA are given in the figure caption. The weight percent for iodinated SF in the figure was corrected from the weight of original SF specimen before iodine treatment. For untreated specimen, there was no abrupt weight loss below 280°C, and the drastic thermal decomposition occurs between 280 and 375°C. This decomposition is associated with the degradation of side chain groups of amino acid residues and the cleavage of peptide bonds of SF main chains.[34] The yield obtained at 800°C for untreated SF was about 30 wt % at a constant heating rate. On

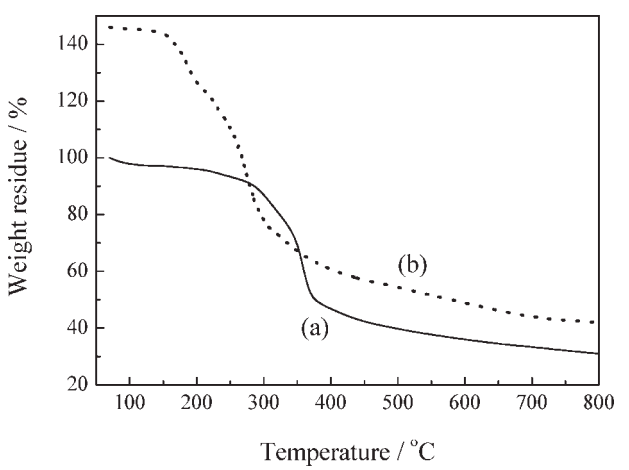

Figure 6 TGA curves of tussah SF fiber: (a) untreated specimen, measured at a heating rate of 5°C and (b) iodinated specimen, measured at $-0.001\%\ s^{-1}$ of weight reduction rate under a constant reaction control mode.

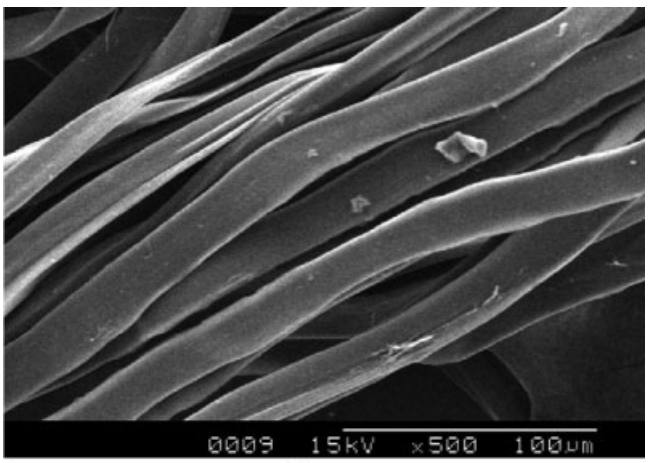

Figure 7 SEM images of carbon fibers prepared from untreated and iodinated tussah SF: (a) untreated specimen; (b) iodinated specimen.

the other hand, the thermal decomposition behavior is influenced by iodine treatment. For iodinated SF, the weight loss was nearly constant to 150°C and the sharp thermal decomposition starts around 150°C. The initial weight decrease is attributed to vaporization of the iodine component in the specimen. The temperature of this first weight loss was higher than that of *B. mori*. This is related to the stronger interaction of iodine component in tussah silk. The slope of TG curve becomes steeper above 270°C where the crosslinking occurs. This is due to thermal degradation of SF accompanied by oxidation reaction by iodine component. Above 380°C, the trend of TG curves for both untreated and iodinated specimens were almost similar each other. The yield obtained at 800°C for iodinated specimen was ca. 42 wt % under dynamic heating condition. The higher yield from iodinated tussah SF would be related to the intermolecular crosslinking of SF by iodination.

Morphological properties

Fiber morphology of carbon fibers prepared from untreated and iodinated tussah SFs was examined by SEM as shown in Figure 7. Nishikawa et al.[27] reported that the carbon fibers prepared from untreated tussah SF by constant heating (10°C min^{-1}) to 800°C were very fragile, swollen, partially melted, and inhomogeneous in appearance, which was originated from much defect formed in the specimen by rapid thermal decomposition of SF molecule. In our defined multistep carbonization process, carbon fibers both from untreated and iodinated SFs were considerably improved and appeared almost homogeneous structure. Particularly, SEM images of iodinated SFs were shown a smoother surface, which may be related to the intermolecular crosslinking of SF caused by iodine treatment.

Structural features

To analyze the structure of carbon fiber FTIR, WAXD, Raman spectroscopy, and elemental composition analysis were carried out. Figure 8 shows FTIR spectra of untreated and iodinated tussah SF fibers heated to different temperatures. The absorption spectrum of untreated specimen exhibits the typical pattern of tussah SF fiber and is characterized by the absorption bands at 1639 cm^{-1}, 1520 cm^{-1}, and 1230 cm^{-1} associated with Amide I, Amide II, and Amide III band of SF molecules, respectively [Fig. 8(a)].[35] The absorption spectrum has been changed because of structural change to increase β-sheet conformation after iodine treatment

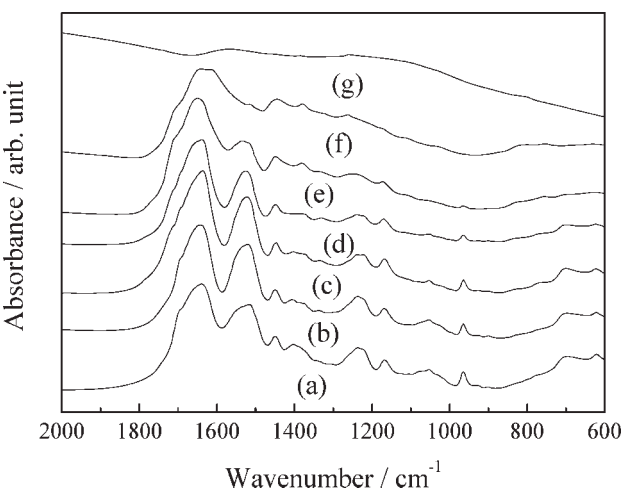

Figure 8 FTIR spectra of iodinated tussah SF heated to different temperatures: (a) untreated specimen, and iodinated specimen heated to, (b) not heated, (c) 260°C, (d) 300°C, (e) 350°C, (f) 435°C, and (g) 800°C.

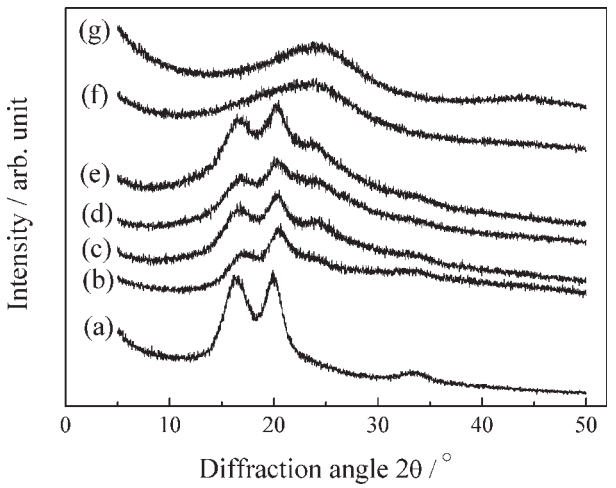

Figure 9 Equatorial WAXD profiles of iodinated tussah SF heated to different temperatures: (a) untreated specimen, and iodinated specimen heated to (b) not heated, (c) 260°C, (d) 300°C, (e) 350°C, (f) 435°C, and (g) 800°C.

[Fig. 8(b)], although it is difficult to recognize it from this figure.[32] The feature of IR spectra of SF molecules was retained below 350°C of heating temperature [Fig. 8(e)]. The bands of SF begin to collapse greatly after heating at 435°C [Fig. 8(f)], and are completely destroyed by carbonization at 800°C [Fig. 8(g)].

Figure 9 shows the WAXD profiles of untreated and iodinated tussah SF fibers heated to different temperatures. Untreated specimen exhibits two peaks at 16.6° ($d = 5.34$ Å) and 20.1° ($d = 4.41$ Å) attributable to 002 and 201 equatorial reflections of the crystalline plane of tussah SF [Fig. 9(a)].[1,36] The iodination causes the change of WAXD profile of the tussah SF crystal, which implies that iodine influences the crystalline structure of the typical β-structure [Fig. 9(b)]. There is no fundamental change of crystalline structure of iodinated SF with the increasing temperature of initial carbonization and the crystalline peaks are visible up to 350°C [Fig. 9(e)]. After carbonized at 435°C [Fig. 9(f)], one broad peak because of typical amorphous structure is shown at $2\theta = 24.0°$ ($d = 3.70$ Å), and the almost same pattern is obtained by heating at 800°C [Fig. 9(g)]. The (002) diffraction of disordered carbon materials appears at $2\theta = 22°$–$25°$[37] and graphite shows a layered structure i.e., the interlayer is separated by a distance of 3.35 Å.[38] Therefore, the diffraction corresponding to *d*-spacing of 3.70 Å is assigned to the diffraction associated with the nongraphite carboneous structure.

To characterize carbon structure Raman spectroscopy was used for the specimens, heated at 800°C. Generally, carbons show mainly two Raman bands, one is at $\sim$ 1580 cm^{-1} and another is at $\sim$ 1360 cm^{-1}. The former corresponds to the E_{2g} mode of graphite, known as graphite peak (G band) and is assigned to the "in-plane" displacement of the carbons strongly coupled in the hexagonal sheets.[39] The latter, which is absent in the single crystal graphite, known as disorder peak (D band) due to discontinuity of hexagonal carbon layer planes such as finite crystallite size and also to edge planes of crystallites.[40] Figure 10 shows the Raman spectra of carbon fibers prepared from untreated and iodinated tussah SF at 800°C. Two broad peaks are shown at 1350 cm^{-1} for D band and at 1580 cm^{-1} for G band. Observed results are plotted with gray closed circles. Black broken and solid lines represent the deconvoluted and total curves, respectively, which were fitted by Gaussian function. Table I represents the peak position, the peak full-width at half-maximum (FWHM) and the integrated intensity ratio of the two peaks (I_G/I_D) obtained from the Gaussian fittings. The spectrum of each sample is broad and is similar to a pattern of diamond-like carbon which possess low crystallinity and mixture of sp^2 and sp^3

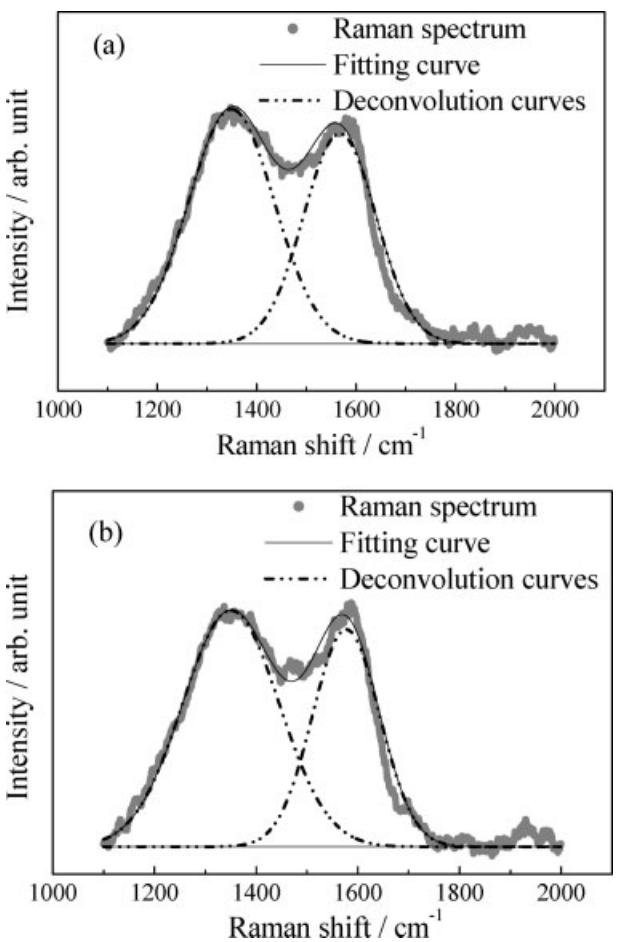

Figure 10 Raman spectra of carbon fibers prepared from untreated and iodinated tussah SF: (a) untreated specimen and (b) iodinated specimen.

TABLE I
Structural Parameters of Carbon Fibers Prepared from Untreated and Iodinated Tussah SF Determined by Raman Spectroscopy

	G band		D band		
Specimen	Peak position (cm^{-1})	FWHM (cm^{-1})	Peak position (cm^{-1})	FWHM (cm^{-1})	I_G/I_D
Untreated SF	1567	172	1349	203	0.89
Iodinated SF	1577	156	1350	223	0.88

carbons. The intensity ratio I_G/I_D of the carbon fibers is almost similar, and the difference in spectra and FWHM is not obviously observed, therefore, the carbon structures of the two fibers are basically same. Figure 11 shows the results of elemental analysis for the carbon fibers prepared at 800°C. For untreated and iodinated specimen, the carbon contents of both are ~ 61 mol %. These less carbon contents are attributed to the existence of various functional groups containing H, N, and O atoms. The carbon content is less and oxygen content is more compared with carbon fibers produced from *B. mori* SF at same temperature.[4] The carbon from *B. mori* shows antibacterial property based on functional groups containing H, N, and O atoms, therefore, antibacterial property is expectative for carbon from tussah SF. From the characterization of carbon structure, it is revealed that the iodine treatment does not enhance the structural characteristics of the carbon fiber, and only controls the thermal degradation behavior of SF.

Tensile properties

To evaluate the mechanical performance of carbon fiber prepared from tussah SF, the tensile strength measurement was performed. Figure 12 shows the stress–strain profiles of carbon fibers prepared from untreated and iodinated tussah SF and the statistical data of the tensile measurements are summarized in Table II. The toughness, ultimate tensile strength, and strain% of carbon fibers prepared from untreated SF were 35.8 J/kg, 14.0 MPa, and 2.8%, respectively. After iodine treatment, the mechanical properties of carbon fiber were considerably increased. The average value of toughness, tensile strength, and strain% of carbon fibers prepared from iodinated specimen were increased to 66.7 J/kg, 17.8 MPa, and 3.3%, respectively. The variations of tensile properties of carbon fibers obtained from iodinated SF were also improved. The higher tensile properties of carbon fibers are caused by both milder carbonization process, which prevents the rapid degradation of SF and the formation of the crosslinking between the adjacent SF molecules in presence of iodine during heating.

CONCLUSIONS

Carbon fibers were produced from natural biopolymer, *A. pernyi* SF fibers treated with iodine vapor at 100°C for 12 h. The highest carbon yield (ca. 39 wt %) was achieved from iodinated tussah SF fibers (cf. ca. 29 wt % of carbon yield for untreated specimen) and the strength of carbon fibers was increased.

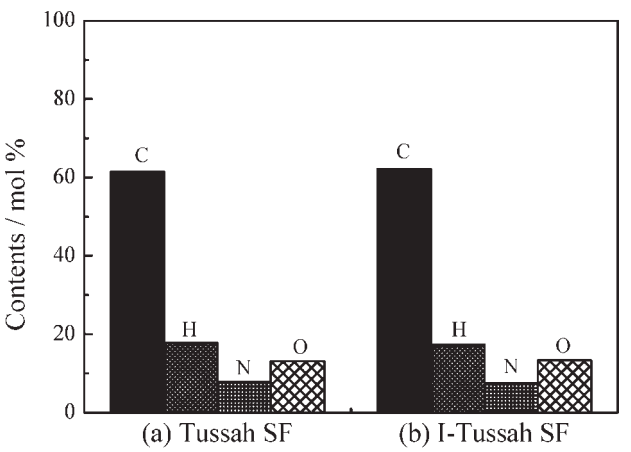

Figure 11 Elemental composition of carbon fibers prepared from untreated and iodinated tussah SF: (a) untreated specimen and (b) iodinated specimen.

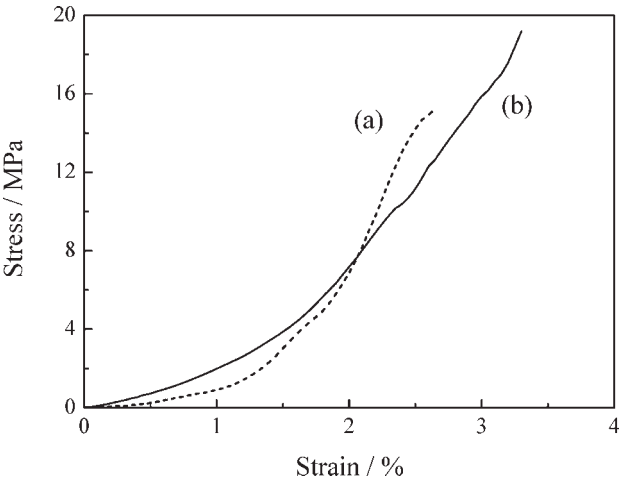

Figure 12 Stress–strain curves of carbon fibers prepared from untreated and iodinated tussah SF: (a) untreated specimen and (b) iodinated specimen.

TABLE II
Statistical Data of the Mechanical Properties of Carbon Fibers Prepared from Untreated and Iodinated Tussah SF

Specimen	Property	Mean value	Standard deviation	Standard error
Untreated SF	Tensile strength (MPa)	14	2.48	0.25
	Strain (%)	2.7	0.55	0.06
	Toughness (J/kg)	36	9.37	0.94
Iodinated SF	Tensile strength (MPa)	18	2.13	0.21
	Strain (%)	3.3	0.54	0.05
	Toughness (J/kg)	67	10.62	1.06

SEM observation showed that the obtained carbon fibers were plain, smooth, and homogenous in appearance, structurally stable, and intact. FTIR, WAXD, and Raman spectroscopy results revealed that the obtained carbon fibers at 800°C from both untreated and iodinated SFs were basically amorphous structure. At the early stage of carbonization of SF, amide bonding was begin to collapse greatly at heating temperatures higher than 350°C and was completely dissociated by carbonization at 800°C. DMTA measurement indicated that at heating above 270°C the iodine component introduced intermolecular crosslinking of SF and the melt flow of the SF was inhibited, which enhances higher carbon yield and better performance of silk-based carbon fiber.

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